Stoichiometric production of aminobenzenes and ketones by photocatalytic reduction of nitrobenzenes in secondary alcoholic suspension of titanium(IV) oxide under metal-free conditions

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ABSTRACT

Photocatalytic conversion of nitrobenzenes in 2-propanol suspensions of bare titanium(IV) oxide (TiO_2) under various conditions was examined. Aniline and acetone were simultaneously produced almost stoichiometrically from a 2-propanol suspension of TiO_2 containing nitrobenzene under deaerated conditions without the use of a precious metal. Nitrobenzenes having another reducible group such as vinyl, chloro and bromo were chemoselectively reduced to corresponding aminobenzenes in 2-propanol suspensions of a TiO_2 photocatalyst with an almost stoichiometric amount of acetone. Photocatalytic reduction of nitrobenzene and oxidation of 2-propanol occurred even in the presence of oxygen, and no re-oxidation of anilines occurred.

1. Introduction

Since photocatalytic reaction of titanium(IV) oxide (TiO_2) satisfies almost all of the 12 proposed requirements for green chemistry [1], organic synthesis of various compounds using TiO_2 photocatalysis has recently been studied by many researchers [2–4]. When TiO_2 is irradiated by UV light, charge separation occurs and thus-formed electrons in the conduction band and positive holes in the valence band cause reduction and oxidation, respectively. This redox reaction proceeds at room temperature and under atmospheric pressure. Since light is indispensable for photocatalytic reaction, the reactions can be easily controlled by the intensity of light and finally can be stopped by turning the light source off. By simple filtration or centrifugation, the TiO_2 photocatalyst is easily separated from the reaction mixture after the reaction. In addition, TiO_2 has been used for a long time as an indispensable inorganic material such as a pigment and UV absorber because it is inexpensive and not toxic for humans and the environment. Although various oxides of titanium exist, TiO_2 in which the oxidation state of titanium is +4 is most stable under the atmosphere and is easily formed without extra attention.

One of the major photocatalytic reductions for organic synthesis with TiO_2 is reduction of nitroaromatics [5–18]. Aminobenzenes synthesized by reduction of corresponding nitrobenzenes are

important compounds as intermediates of various useful compounds such as dyes and medicines [19]. Photocatalytic reduction for organic synthesis has been carried out in the presence of an electron donor, such as methanol or triethanolamine, and in the absence of oxygen (O_2). The purpose of the electron donor is to scavenge holes and to reduce recombination of holes and electrons in and/or on the particles. Since reduction of nitrobenzene competes with reduction of O_2, photocatalytic reduction has been carried out under deaerated conditions. In our previous paper, we reported photocatalytic reduction of nitrobenzenes to corresponding aminobenzenes in an aqueous suspension of TiO_2 in the presence of oxalic acid (OA) or formic acid (FA) as a hole scavenger [16,17]. We also examined the photocatalytic reduction of nitrobenzenes having other reducible groups using a simple photocatalyst, TiO_2, in the presence of OA as a hole scavenger at room temperature and atmospheric pressure, and we found that only the nitro group was chemoselectively reduced to an amino group and that aminobenzenes with reducible groups such as *m*-aminovinylbenzenes were obtained in high yields without using precious metals or high-pressure gaseous reducing reagents (Scheme 1) [18].

In the photocatalytic reduction of nitrobenzenes, positive holes in the valence band were effectively removed by FA and OA. These hole scavengers are "greener" sacrificial reagents because they are easily oxidized into carbon dioxide (CO_2) and thus-formed CO_2 molecules are removed from the liquid phase in the presence of organic acids. The photocatalytic reduction of nitrobenzenes would be more attractive if positive holes are utilized for synthesis of
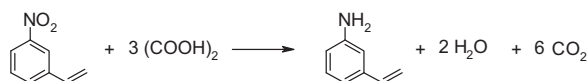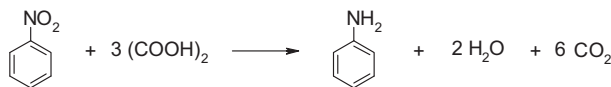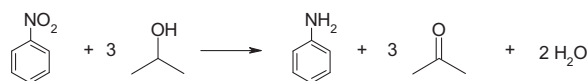
Scheme 1.

Scheme 2.

Scheme 3.

valuable compounds, not for fruitless degradation or mineralization. Utilization of positive holes enables simultaneous production of two valuable reduced and oxidized compounds. In the case of reduction of nitrobenzene using OA (Scheme 2), atom efficiency (AE) [20], which is defined as Equation 1, is calculated to be 23.7%.

$$\text{Atom efficiency} (\%) = \frac{(\text{molecular weight of the desired product})}{(\text{sum total of molecular weights of all substances produced})} \times 100 \quad (1)$$

The photocatalytic reduction of nitrobenzenes to aminobenzenes using OA or FA is "green" from the viewpoint of practical operation for reasons stated above; however, the AE of the reaction is not high because positive holes are consumed only for mineralization of the hole scavengers and large amounts of CO_2 (six-times larger than the amount of aminobenzenes) and water (twice the amount of aminobenzenes) are formed. Therefore, atom efficiency should increase if positive holes are utilized for production of valuable compounds, not for fruitless mineralization, during the reduction of nitrobenzenes by photogenerated electrons. In this study, we examined photocatalytic reduction of nitrobenzenes to aminobenzenes in secondary alcohols. Secondary alcohols are regarded as a model raw material of carbonyl compounds and work as hole scavengers and solvents. Since carbonyl compounds such as aldehydes and ketones are precursors for many drugs, vitamins and fragrances, selective oxidation of alcohols to carbonyl compounds is one of the most important transformations in industrial and fundamental chemistry [21,22]. Therefore, several photocatalytic methods for selective oxidation of alcohols to corresponding carbonyl compounds have been reported [23–30]. Here we report 1) stoichiometry of products, i.e., aminobenzenes and carbonyl compounds, in the photocatalytic reaction, 2) chemoselective reduction of nitrobenzene having reducible groups such as m-nitrovinylbenzene to m-aminovinylbenzene and 3) effects of the presence of O_2 and type of TiO_2 on nitrobenzene formation.

2. Experimental

All of the reagents were commercial materials of reagent grade (Wako Pure Chemical) and used without further purification except for 2-propanol, which was dehydrated with a molecular sieve 4A. A typical procedure is as follows. Bare TiO_2 powder (50 mg) was suspended 5 cm³ of 2-propanol containing nitrobenzene (50 μmol) in a test tube. The tube was sealed with a rubber septum and then photoirradiated by a high-pressure mercury arc (Eiko-sha, 400 W, λ > 300 nm) under argon (Ar) with magnetic stirring at 298 K. After the reaction, gas phase was analyzed by a gas chromatograph (Shimadzu, GC-8A equipped with Molecular Sieve 5A columns). After the suspension had been filtered to remove particles, the amounts of nitrobenzenes remaining and product(s) were determined by a gas chromatograph (Shimadzu GC-2025 equipped with DB-1 columns and Shimadzu GC-14B equipped with PEG 20M columns). To obtain apparent quantum efficiency (AQE), UV light-emitting diode (UV-LED, POT-365, Asahi Spectra Co., Ltd., Tokyo, maximum energy at λ = 365 nm) was used as light source. Light intensity of the

UV-LED was measured using a spectroradiometer USR-45D (Ushio, Tokyo).

3. Results and discussion

3.1. Stoichiometric production of aniline and acetone in photocatalytic reaction of nitrobenzene in 2-propanol suspension of TiO2 under deaerated conditions

Photocatalytic reaction of nitrobenzene in a 2-propanol suspension of rutile-type TiO_2 (Tayca, MT-150A) with irradiation of UV light was examined under deaerated conditions. Expected stoichiometry of this reaction is shown in Scheme 3 and AE of this reaction is calculated to be 88.1%, in which acetone is regarded as a desired product.

The value was larger than that of reduction of nitrobenzene with OA (Scheme 2) because no CO_2 was formed in the reduction in 2-propanol (Scheme 3). Fig. 1 shows time courses of nitrobenzene remaining, aniline formed and acetone formed in a 2-propanol suspension of TiO_2 (Tayca, MT-150A) for 30-min photoirradiation under deaerated conditions. Just after photoirradiation, nitrobenzene monotonously decreased, while aniline and acetone were formed as the reduction product of nitrobenzene and the oxidation product of 2-propanol, respectively. After 15-min photoirradiation,
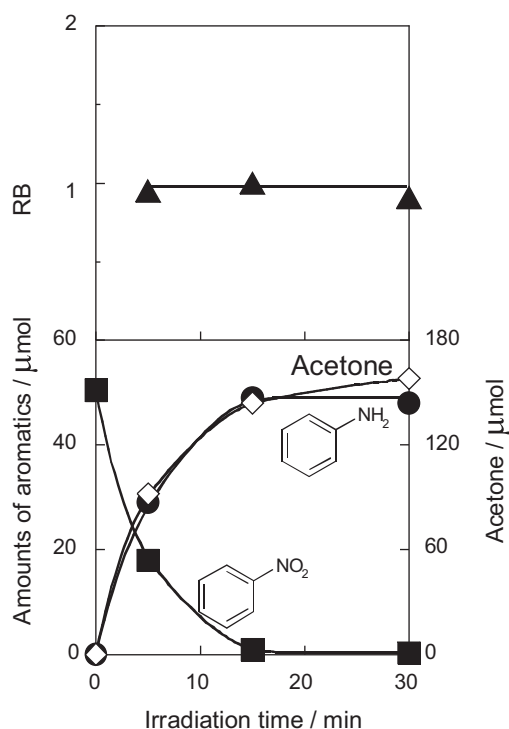
Fig. 1. Time courses of amounts of nitrobenzene remaining (squares), aniline formed (circles) and acetone formed (diamonds) and RB of aniline and acetone (triangles) in photocatalytic reaction of nitrobenzene in 2-propanol suspensions of TiO_2 under deaerated conditions.

nitrobenzene was almost completely consumed and aniline was obtained in a high yield (98%). We noted that the aniline that had been formed was not re-oxidized even by excessive photoirradiation after complete consumption of nitrobenzene. This result indicates that no re-oxidation of aniline by holes occurred in the presence of a large excess of 2-propanol. After nitrobenzene had been consumed, a small amount of acetone was formed and the color of TiO_2 became blue, indicating that a apart of Ti^{4+} in TiO_2 was reduced to Ti^{3+} along with oxidation of 2-propanol to acetone. To evaluate stoichiometry of the reaction in the present conditions, a new indicator, i.e., redox balance (RB), was used. Since reduction of nitrobenzene to aniline and oxidation of 2-propanol to acetone require six electrons and two holes, respectively, RB was calculated from Equation 2 and values of RB are also shown in Fig. 1.

$$RB = \frac{6 \times \text{amount of aniline}}{2 \times \text{amount of acetone}} \quad (2)$$

The values of RB were almost unity at 5 min and 15 min, indicating that the reaction proceeded stoichiometrically according to Scheme 3, i.e., generated electrons and holes were selectively used only for reduction of nitrobenzene to aniline and oxidation of 2-propanol to acetone, respectively. Due to the formation of a small amount of acetone, the value of RB was slightly decreased at 30 min. From the ratio of the amount of aniline and the amount of photons irradiated (Eq. (3)), AQE was calculated to be 89% at 10-min irradiation by UV-LED.

$$AQE(\%) = \frac{6 \times \text{amount of aniline}}{\text{number of incident photons}} \times 100 \quad (3)$$

3.2. Chemoselective reduction of nitrobenzenes to aminobenzenes having reducible groups in 2-propanol suspension of TiO_2 under deaerated conditions

Photocatalytic stoichiometric formation of aniline and acetone was expanded to chemoselective reduction of nitrobenzenes to aminobenzenes having reducible groups (vinyl, chloro and bromo groups) along with oxidation of 2-propanol to acetone. Fig. 2 shows time courses of m-nitrovinylbenzene (NVB) remaining, m-aminovinylbenzene (AVB) formed and acetone formed in a 2-propanol suspension of TiO_2 (MT-150A) for 30-min photoirradiation under deaerated conditions. Just after photoirradiation, the amount of NVB monotonously decreased and NVB was almost completely consumed after 15 min, while AVB was obtained in a high yield (>99%) as the reduction product of NVB. Other reduced products (nitroethylbenzene and aminoethylbenzene) were not formed. The high yield of AVB indicates that neither reaction of the benzene ring, reduction of the vinyl group nor re-oxidation of the amino group of AVB occurred in the present system. Scheme 4 shows the expected stoichiometry of photocatalytic simultaneous formation of AVB and acetone by reduction of NVB and oxidation of 2-propanol under the present conditions.

After NVB had been consumed, a small amount of acetone was formed and the color of TiO_2 became blue as in the case of nitrobenzene, indicating that a part of Ti^{4+} in TiO_2 was reduced to Ti^{3+}. However, Ti^{3+} species was easily oxidized to Ti^{4+} because the color became white after exposing the suspension to air. The values of RB were almost unity at 5 min and 10 min, indicating that the reaction proceeded stoichiometrically according to Scheme 4, i.e., generated electrons and holes were selectively used only for reduction of NVB to AVB and oxidation of 2-propanol to acetone, respectively.

Applicability of the stoichiometric chemoselective reduction was investigated using nitro compounds having other reducible groups (chloro and bromo groups), and Table 1 shows results of the photocatalytic chemoselective reduction of these nitrobenzenes in a 2-propanol suspension of TiO_2 particles under deaerated
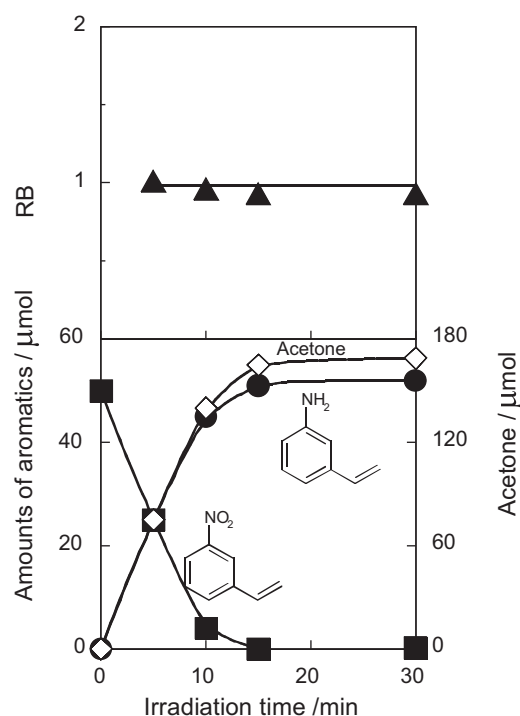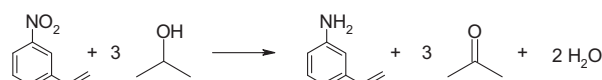

Fig. 2. Time courses of amounts of NVB remaining (squares), AVB formed (circles) and acetone formed (diamonds) and RB of AVB and acetone (triangles) in photocatalytic reaction of NVB in 2-propanol suspensions of TiO_2 under deaerated conditions.

Scheme 4.

Table 1
Photocatalytic chemoselective reduction of nitrobenzenes to corresponding aminobenzenes in 2-propanol suspensions of TiO_2 and redox balance of aminobenzenes and acetone under deaerated conditions[a].

Substrate	Product	Conv./%	Sel./%	RB[b]
NO₂ ... (vinyl)	NH₂ ... (vinyl)	92	98	0.96
NO₂ ... Cl	NH₂ ... Cl	>99	82	0.84
NO₂ ... Br	NH₂ ... Br	86	>99	0.94

[a] Nitrobenzenes: 50 μmol, 2-propanol: 5 cm³, TiO_2: MT-150A (50 mg), Photoirradiation: 10 min.
[b] Redox balance defined as [3 × (amount of aminobenzene)/(amount of acetone)].

conditions. Only the nitro group of these compounds was chemoselectively reduced even in the presence of chloro and bromo groups, resulting in the formation of corresponding amino compounds with high yields. Since the values of RB were close to unity, stoichiometric reduction of nitrobenzenes and oxidation of 2-propanol occurred under the present conditions. These results indicate wide applicability of this photocatalytic method for chemoselective reduction of a nitro group to an amino group and stoichiometric formation of acetone without using precious metals and H_2. The reaction tendency of 4-chloronitrobenzene was slightly different from that of 4-bromonitrobenzene, i.e., 4-chloronitrobenzene exhibited high conversion and low selectivity while 4-bromonitrobenzene exhibited low conversion and high selectivity. It is difficult to explain these results because by-product(s) was not determined in this reaction condition. Change in the reaction condition might be required to discuss the effect of halogen on the reaction rate and selectivity.

3.3. Stoichiometric production of aniline and acetone in photocatalytic reaction of nitrobenzene in 2-propanol suspension of TiO_2 under air

When photocatalytic reaction is applied for reduction of a substrate, oxygen is generally removed from the reaction system because oxygen always acts as strong acceptor of photogenerated electrons and decreases the efficiency of photocatalytic reduction in the target. To remove the negative effect of O_2, photocatalytic reduction has been performed under vacuum or under inert gases such as nitrogen and argon. However, removal of O_2 by vacuuming or replacing with these gases requires great care and consumes a large amount of energy. Reactions under air, i.e., reactions free from any additional operations, are most favorable from the viewpoint of practical application. In this study, photocatalytic reaction of nitrobenzene in a 2-propanol suspension of TiO_2 was carried out under air to examine whether stoichiometric production of aniline and acetone was achieved or not, and the results are shown in Fig. 3. As well as results under deaerated conditions (Fig. 1), just after photoirradiation, nitrobenzene decreased monotonously, while aniline was formed and the yield of aniline reached 96%, indicating that reduction of nitrobenzene occurred even in the presence of O_2 and the rate was almost the same in the absence of O_2. It should be noted that no aniline was re-oxidized with prolonged photoirradiation even in the presence of O_2. Since the yield of acetone was larger than that of aniline and the value of RB was smaller than unity, fruitless oxidation of 2-propanol with O_2 (Scheme 5) partly occurred.

From the results in the presence of O_2, it can be concluded that 1) reduction of nitrobenzene (electron trapping by nitrobenzene) was hardly affected by the presence of O_2 and 2) electron trapping by O_2 occurred additionally and, therefore, the yield of acetone increased.

3.4. Effect of kinds of TiO_2

Table 2 shows results of simultaneous production of aniline and acetone in 2-propanol suspensions of various commercial TiO_2 photocatalysts. In all cases, nitrobenzene was consumed, and aniline and acetone were obtained. Among the samples, rutile-type TiO_2 samples (Japan Reference Catalyst TIO-6 supplied by Catalysis Society of Japan and MT-150A) exhibited higher conversion of nitrobenzene and higher selectivity of aniline (Entries 1 and 2). In addition, values of RB were almost unity in these samples, indicating that only the reaction shown in Scheme 3 occurred, i.e., neither a side reaction nor a successive reaction consuming aniline and acetone occurred. On the other hand, anatase-type TiO_2 sample (ST-01) and anatase-rutile-mixed TiO_2 sample (P 25) exhibited slightly smaller nitrobenzene conversion, aniline selectivity and
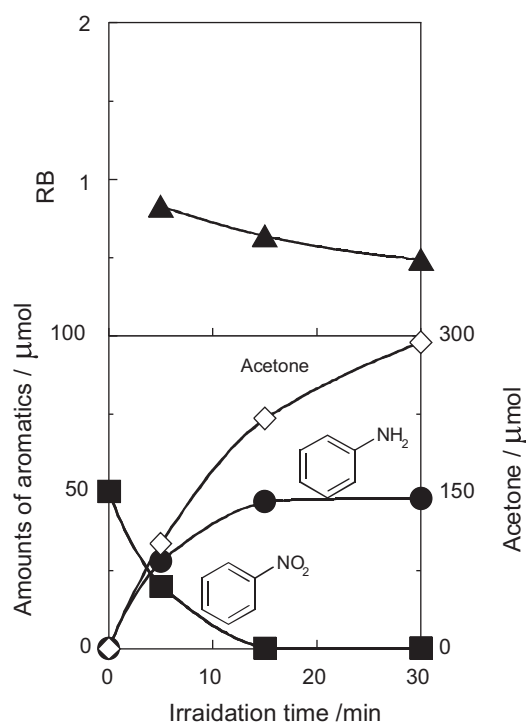

Fig. 3. Time courses of amounts of nitrobenzene remaining (squares), aniline formed (circles) and acetone formed (diamonds) and RB of aniline and acetone (triangles) in photocatalytic reaction of nitrobenzene in 2-propanol suspensions of TiO_2 under air.

Scheme 5.

RB (Entries 3 and 4). The results for these four samples suggest that rutile structure was appropriate for simultaneous production of aniline and acetone. One of the apparent differences between anatase-type TiO_2 and rutile-type TiO_2 is potential of the conduction band (-0.3 V in anatase and 0 V in rutile vs. SHE). Anatase-type TiO_2 may induce another reductive reaction that cannot be induced by electrons in the conduction band of rutile-type TiO_2. Relatively low selectivity was observed when ST-01 was used as TiO_2, indicating that side-reaction(s) occurred. In photocatalytic reduction of nitrobenzene in the presence of other hole scavengers [17,18], ST-01 exhibited almost same results. Specific surface area and crystallinity of TiO_2 may affect the reaction rate and selectivity. Large surface area increases active site and substrate adsorption whereas high crystallinity decreases possibility of recombination of electron

Table 2
Effects of TiO_2 on conversion of nitrobenzene, selectivity of aniline and RB of aniline and acetone in reduction of nitrobenzene in 2-propanol suspensions of TiO_2 under deaerated conditions[a].

Entry	TiO_2[b]	S_{BET}[c]/$m^2 g^{-1}$	Phase[d]	Conv./%	Sel./%	RB[e]
1	MT-150A	101	R	99	98	1.00
2	JRC-TIO-6	80	R	98	97	0.97
3	ST-01	260	A	80	75	0.86
4	P 25	49	A, R	90	83	0.86

[a] Nitrobenzene: 50 μmol, 2-propanol: 5 cm^3, TiO_2: 50 mg, Photoirradiation: 15 min.
[b] MT-150A, ST-01 and P 25 were supplied from Tayca, Ishihara and Degussa, respectively. JRC-TIO-6: Japan Reference Catalyst of Catalysis Society of Japan.
[c] Specific surface area calculated by BET method.
[d] R: Rutile, A: Anatase.
[e] Redox balance defined by Eq. (2).

and positive hole. Therefore, photocatalyst having large surface area and low crystallinity such as ST-01 may cause side-reactions such as coupling of nitro compounds and suffer surface poisoning due to high concentration of nitrobenzene and its reduction intermediates.

4. Conclusions

Photocatalytic reduction of nitrobenzenes to corresponding aminobenzenes in 2-propanol suspensions of titanium(IV) oxide (TiO$_2$) under various conditions was examined and the following results were obtained.

(1) Nitrobenzene was quantitatively converted into aniline under deaerated conditions with an almost stoichiometric amount of acetone as an oxidation product of 2-propanol. After consumption of nitrobenzene, aniline formed did not decrease and a small amount of acetone was formed with change of TiO$_2$ color to blue, indicating that part of Ti^{4+} in TiO$_2$ was reduced to Ti^{3+} along with 2-propanol oxidation.
(2) Only the nitro group of nitrobenzenes having other reducible groups was chemoselectively reduced in 2-propanol suspensions of TiO$_2$ under deaerated conditions. *m*-Nitrovinylbenzene (NVB) was reduced to *m*-aminovinylbenzene (AVB) with stoichiometric production of acetone as in the case of (1). With further photoirradiation after consumption of NVB, no re-oxidation of AVB occurred. Applicability of the photocatalytic chemoselective reduction in a 2-propanol suspension was investigated using halogenated (chloro- or bromo-) nitrobenzenes and only the nitro group was reduced to an amino group without reductive dehalogenation.
(3) In the photocatalytic reduction of nitrobenzene in a 2-propanol suspension, aniline is obtained in high yields even in the presence of dioxygen (O$_2$), i.e., free from gas-phase control. After consumption of nitrobenzene, only acetone was formed without decrease of aniline along with photoirradiation, indicating that simple mineralization of 2-propanol occurred; holes oxidized 2-propanol to acetone and electrons were trapped by O$_2$, and the thus-formed activated O$_2$ also oxidized 2-propanol, not aniline.

Acknowledgements

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